## **Supporting information**

## Li<sub>2</sub>O reinforced Cu nano-clusters as porous structure for Dendrite-free and Long-lifespan lithium metal anode

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Figure S1. BET measurement for the bare Cu, Cu-NC/Cu and CuO-NC/Cu electrodes.



**Figure S2.** CV curves of (a) the CuO-NC/Cu electrode (the 1st reduction sweep corresponds to the reduction of the CuO nano-clusters) and (b) the bare Cu electrode. The voltage sweep rate was 0.05 mV s<sup>-1</sup> between 0 and 2 V vs Li/Li<sup>+</sup>.



**Figure S3.** XRD of the CuO-NC/Cu electrode before and after the electrochemical reduction of the CuO nano-clusters. The disappearance of the cupric oxide phase (JCPDS card No. 41-0254) justified the reduction of CuO nano-clusters. The weak signal of  $Li_2O$  after the reduction should be due to the co-formation of  $Li_2O$  and SEI layer at the close reductive potential area that affects the crystal phase of  $Li_2O$ .



**Figure S4.** O 1s and Li 1s XPS spectra of the CuO-NC/Cu electrode before and after the electrochemical reduction of the CuO nano-clusters.



**Figure S5.** 3D AFM images of CuO-NC/Cu electrode before/after reduction of the CuO nanoclusters.



**Figure S6.** (a) Cross section of the CuO-NC/Cu electrode after the 1st cycle for the CuO reduction; (b) Top view of the CuO-NC/Cu electrode after long cycling with high capacity loading of 4 mAh cm<sup>-2</sup>.



**Figure S7.** SEM images of (a) the burned CuO layer, (b) the surface modified Cu substrate after the electrochemical reduction of the burned CuO layer and (c) the dead Li after the cycling test; (d) Charge-discharge profiles of the burned CuO electrode; (e) Coulombic efficiency in Cu/Li cells with the surface modified Cu substrates derived from CuO nano-clusters and burned CuO layer.